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Effects of Acid Digestion on the Peak Decomposition and Impact Sensitivity of Nitrocellulose

by William M. Sherrill

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William M. Sherrill
Weapons and Materials Research Directorate, ARL

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<p>14. ABSTRACT Cellulose obtained from commercially available cotton balls was acid digested with hydrochloric acid at various times and then nitrated with a nitrating acid mixture to produce acid-digested nitrocellulose. Samples of this material were analyzed to determine the effect, if any, of acid digestion on peak decomposition and sensitivity to impact when compared to an undigested sample of nitrocellulose produced from the same cellulose source.</p>				
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1. Introduction

Cellulose is an important product with global annual production exceeding 7.5×10^{10} tons (1). While it has primarily found uses in many aspects of everyday life, it also has had a profound effect on military energetic materials with the discovery of nitrocellulose in 1845 by the German chemist Schönbein (2). Its discovery made the transition from black powder to smokeless propellants possible and was a tremendous leap forward in the energetic technology of that era (3).

In the 1950's it was discovered that by digesting cellulose in sulfuric acid, it is possible to make a suspension of cellulose particles which have properties differing greatly from those of the parent material (4–6). This digested material was found to be crystalline particles of cellulose left behind after the hydrolysis of the amorphous portions of the cellulosic polymer. After homogenization, these typically are less than 100 nm in total length and have been referred to as cellulose nanocrystals or nanocellulose (7).

With the inherent particle size differences between the cellulose nanocrystals and naturally occurring cellulose, there would be advantages to having nitrocellulose with a smaller particle size over nitrating naturally occurring cellulose. What is described in this report is a method for the production of acid digested nitrocellulose by pre-digesting cellulose before the nitration is carried out. The properties of this material are evaluated and compared to a sample of lab prepared nitrocellulose to evaluate its physical characteristics, such as particle size, nitrogen content, and sensitivity to impact.

2. Experimental

All cellulose for this work was obtained from commercially available cotton balls. Depending on the source and purity of the cotton, as well as the method of digestion used, the average particle size for the crystals varies widely (7). There are differing methods for the acid digestion of cellulose with the primary methods being the treatment with dilute mineral acids such as hydrochloric (HCl) (8) or sulfuric (H₂SO₄) (9, 10). For this study, it was desirable to use the HCl method of digestion in order to have the free hydroxyl groups left on the cellulosic particles after the completion of the digestion. After neutralization and drying of the digested material, this allowed for the direct treatment of the particles with a nitrating acid mixture without interference from sulfate groups that would be left behind after an H₂SO₄ digestion.

Based on the scanning electron microscope (SEM) images, there is a significant difference in the particle size and morphology depending not only on whether the material has been acid digested,

but also on the duration of the digestion. Cotton in its natural fiber state consists of long fibrils as depicted by the SEM image of undigested cotton in figure 1. Four-hour digested, unhomogenized cotton appears to be shorter versions of the fibrils observed in naturally occurring cotton with the diameter of the fibrils being roughly the same as in the natural state. In the case of the 12-h digestion with acid, the fibrils have undergone more decomposition although it is still possible to observe short portions of them approximately 300 μm in length (figure 1). The remainder of the overnight digested material has lost most of its fibril morphology and instead adopted either a rod or plate-like morphology.

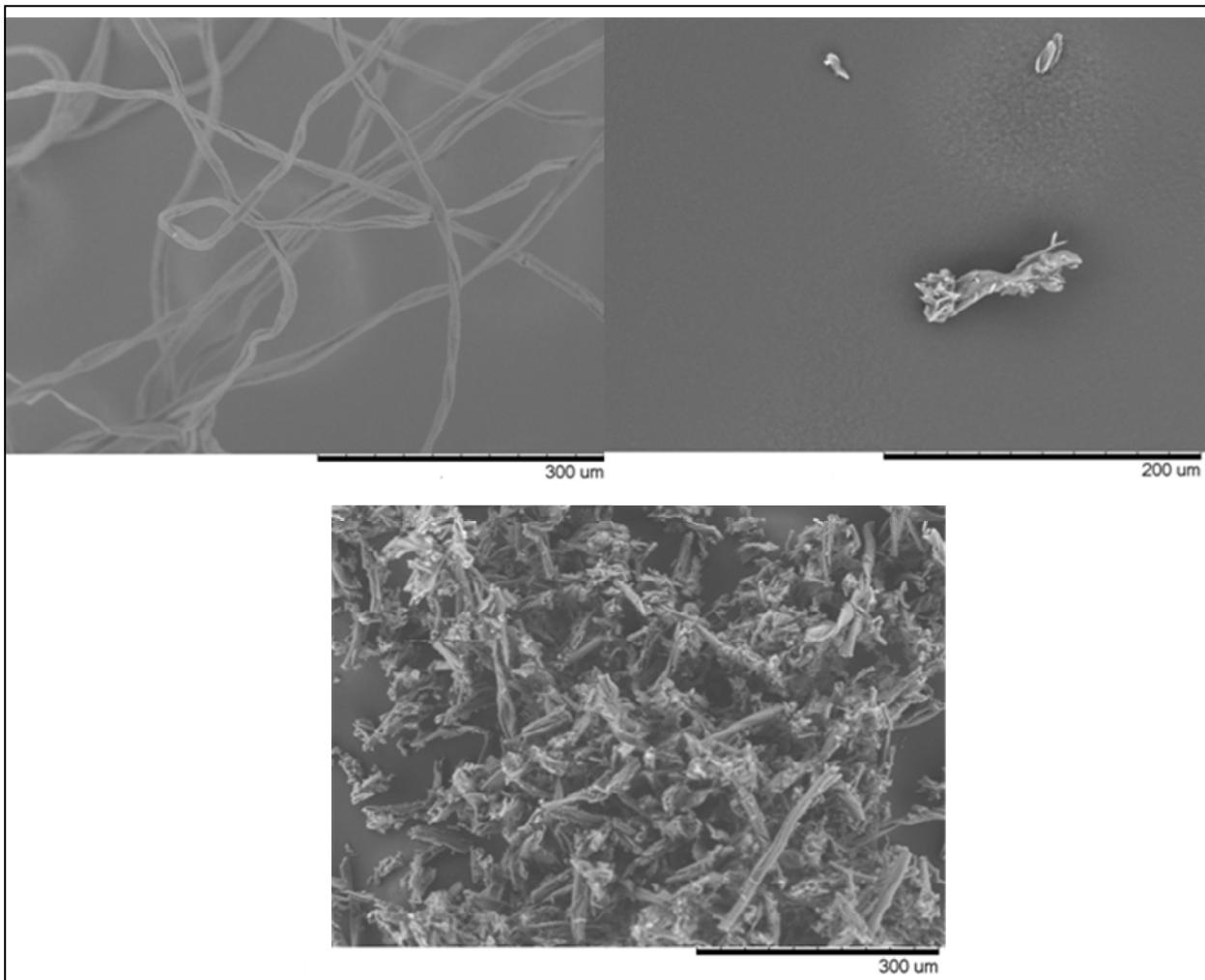


Figure 1. SEM images of cotton (clockwise from top left): 100% cotton undigested, 100% cotton 4-h digestion, and 100% cotton overnight (18-h) digestion.

Nitration of the material was carried out with the aid of a 50/50 volume mixture of 98% H_2SO_4 /70% nitric acid (HNO_3). SEM images of the nitrated materials show little change in the nitrated material from that of the undigested cotton ball sample. For both the 4-h digested nitrocellulose (4DNC) and the overnight digested nitrocellulose (18DNC), nitration of the digested cotton lead to the formation of agglomerates of smaller particles with very uneven and rough surface characteristics (figure 2).

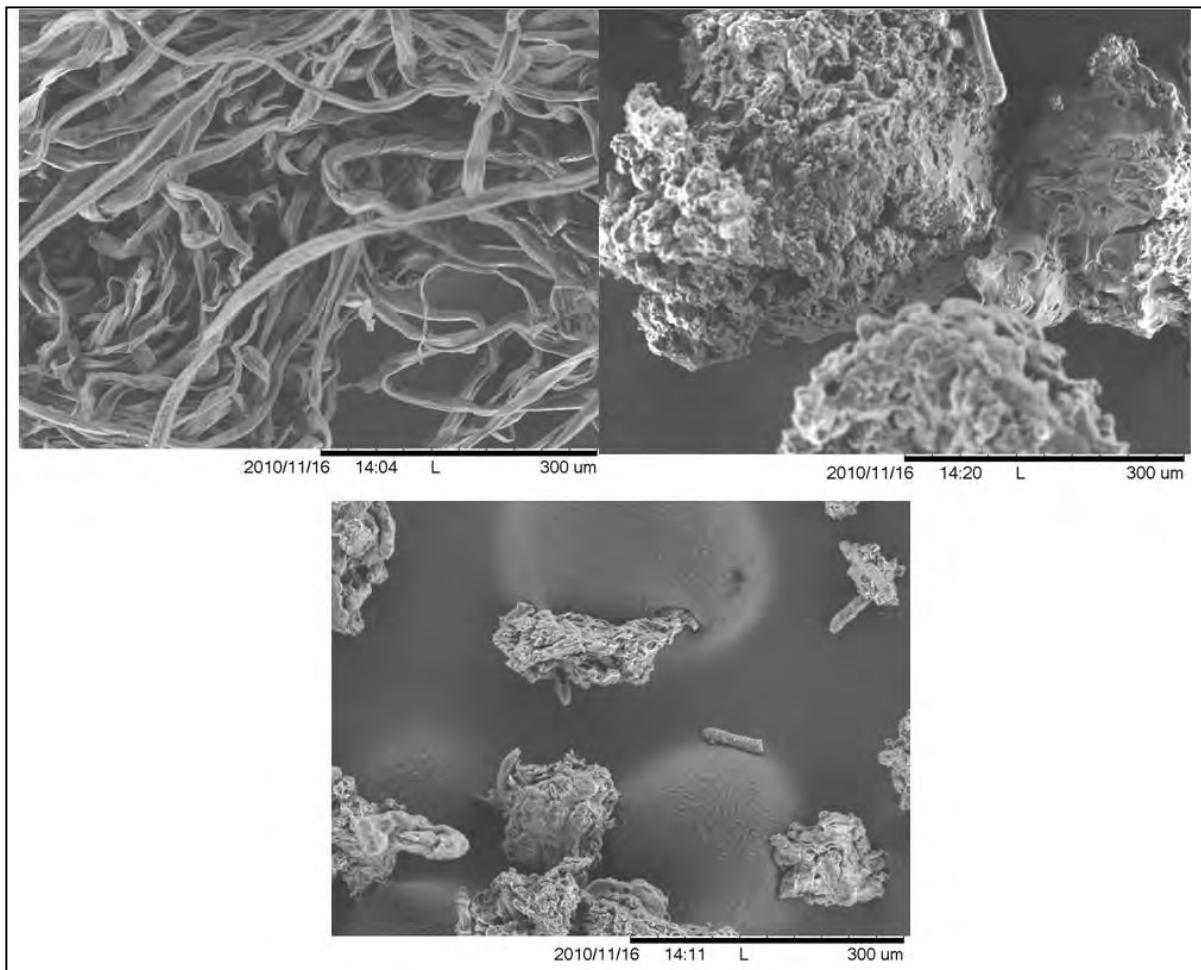


Figure 2. SEM images of nitrated cellulose (clockwise from top left): nitrocellulose, 4DNC, and 18DNC.

With the nitrated materials in hand, the percent nitrogen content of each sample was derived from bomb calorimetry experiments. From these experiments, nitrocellulose obtained from the nitration of natural cotton fibers (NC) was found to have an average heat of combustion over three runs of 2308 cal/g, 4DNC released 2299 cal/g, and 18DNC 2242 cal/g. A calibration plot was generated by plotting the literature values for the heat of combustion for samples of a known percent nitrogen composition versus the percent nitrogen in the sample; 0% (determined in this study), 12.6% (11), 13.45% (11), and 14.14% (11) (figure 3). The resulting graph yielded a straight line, making it reasonable to determine the estimated nitrogen content of the NC, 4DNC, and 18DNC samples without the need of a $\text{FeCl}_2\text{-TiCl}_3$ titration (12, 13). While other methods for nitrogen content determination are known, see Norwitz and Chasan (14). Based on the equipment available, combustion analysis was deemed to be the most appropriate means of nitrogen content analysis for this study. Using the plot shown in figure 3, the heat of combustion

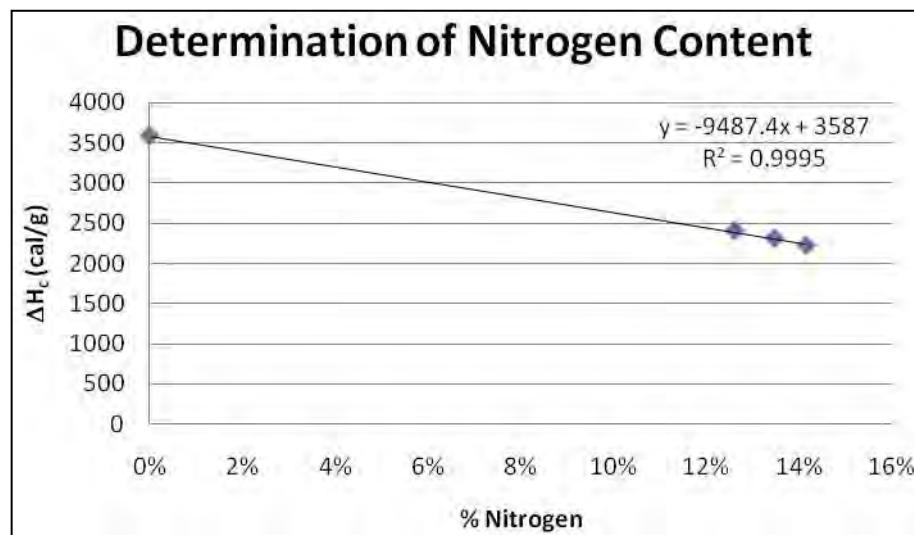


Figure 3. Plot of ΔH_c vs. nitrogen percentage showing linear regression analysis.

values translated to an approximate nitrogen content of 13.47% for NC, 4DNC gave approximately 13.58% and the 18DNC approximately 12.02%.

The decomposition temperatures for each of the samples were determined using differential scanning calorimetry (DSC). Using a heating rate of 10 °C per min and an average of three runs, it was found the NC decomposed at 201.18 °C, the 4DNC decomposed at 203.56 °C and the 18DNC decomposed at 210.33 °C. The overall trend seen in this study is the higher the percent nitrogen incorporation into the sample, the lower the peak decomposition temperature. This finding agrees with what has been published recently in the literature (15). It is interesting to note that while the percent nitrogen of the NC and 4DNC samples was found to be similar; the difference in the peak decomposition is 2 °C higher for the digested sample than for NC.

3. Experimental Procedures

3.1 Acid Digestion

3.1.1 Four-Hour Digested Cotton Balls (General Procedure)

A mass of 5.014 g of 100% cotton, U.S. Cotton LLC cotton balls that had been “fluffed” by pulling apart, a stir bar, and 44 mL of 4M HCl was added to a 250 mL round bottom flask. The flask was sealed with a rubber septum and vented with a hypodermic needle. This was allowed to stir at 80 °C for 4 h, at which point the cotton had been digested enough to be an easily stirred slurry. This slurry was diluted with 50 mL of ethanol and filtered. It was rinsed twice with 25-mL portions of ethanol and finally with a 25 mL portion of diethyl ether. The filter cake was removed and allowed to dry. (To speed up the drying process, the material can be dried for

several hours in a vacuum oven set at 60 °C at 0 torr until constant mass is achieved.) The yield on this process was 4.8972 g of white powdered cotton.

3.1.2 Overnight Digested Cotton Balls

A sample of U.S. Cotton LLC “fluffed” 100% cotton balls with a mass of 5.038 g was added to a 250-mL round bottom flask and was digested according to the general procedure except the cotton was allowed to stir 18 h at 80 °C. Total yield on this procedure was 3.9814 g of white powdered cotton.

3.2 Nitration

Note that mixing concentrated H_2SO_4 and concentrated HNO_3 is an exothermic process which can result in boiling of the solution if mixed too rapidly. These solutions also emit a significant portion of toxic as well as caustic fumes and must be mixed slowly, with adequate cooling, in a fume hood.

3.2.1 Nitration of Cotton Balls (NC) (General Procedure)

A sample with a mass of 5.0341 g of “fluffed” 100% cotton, U.S. Cotton LLC. cotton balls was added to a beaker containing a mixture of 10 mL 95% H_2SO_4 and 20 mL 70% HNO_3 which had been cooled to 10 °C in an ice bath. Once the acid had completely coated the cotton, it was allowed to soak at room temperature for 30 min with stirring approximately every 5 min, at which point it was removed from the acid, and any excess acid was allowed to drain. Any residual acid in the cotton was neutralized by plunging the cotton into a solution of saturated sodium bicarbonate ($NaHCO_3$) until no more CO_2 was evolved. It was removed from the $NaHCO_3$ solution and washed three times with 50 mL portions of distilled H_2O and spread out over a string in the fume hood and allowed to dry overnight at room temperature. The process yield was 4.9879 g of an off-white powder.

3.2.2 Nitration of Overnight Digested Cotton Balls (18DNC)

The clumps of dried cotton from the acid digestion procedure were broken up using an agate mortar and pestle. This was then passed through sieve screens using a sonic sifter fitted with consecutive screens with particle sizes of 500, 355, and 125 μm . The sifter was set on the low setting and allowed to run for 10 min. After which, any material remaining on the screening was again broken up with the agate mortar and pestle and the procedure was repeated until there was no material remaining on the screens. The amount of material recovered after sieving was 3.5340 g. This material was then nitrated according to the general nitration procedure previously described. The digested cotton was added portion wise to the nitrating acid mixture at room temperature and was manually stirred for 15 min and allowed to sit for another 15 min. After the allotted time had passed, the entire contents of the nitrating bath were transferred to a saturated solution of $NaHCO_3$ in water (~50 g in 25 mL of H_2O). *Note: Due to the small particle size of the digested nitrocellulose and the large volume of CO_2 produced, there is a tremendous amount*

of foam generated. It is recommended the NaHCO₃ be placed in an overly large container and the acidified cotton be added slowly to minimize any overflow. Once the solution had been neutralized and no further evolution of CO₂ was observed, the digested NC was filtered using a Buchner funnel, washed twice with 25 mL of H₂O and once with 25 mL of ether. The filter cake was then oven dried at 60 °C in a vacuum oven at 0 torr until no mass change was observed between weighings (~3 h). Yield 3.3421 g of an off-white powder.

3.2.3 Nitration of Four-Hour Digested Cotton Balls (4DNC)

A mass of 4.8972 g of cotton digested for 4 h in HCl was nitrated according to the general nitration procedure previously given. The mixture was allowed to stir for 30 min at room temperature at which point it was quenched using an excess of saturated NaHCO₃, diluted with 100 mL of ethanol and filtered. The filter cake was washed twice with 25-mL portions of ethanol and once with a 25-mL portion of ether. The cake was allowed to dry overnight at room temperature. The amount of material recovered was 4.5674 g of an off-white powder.

3.3 Approximate Heat of Combustion

Heat of combustion (ΔH_c) data for samples was acquired with a Parr model 6200 Bomb calorimeter equipped with a Parr 6510 water handling system. Samples were combusted as a loose powder in a Parr 1108 stainless steel oxygen bomb. Approximately 10 cm of Parr bomb fuse wire was used for each run and the bomb was charged with 40 PSI of O₂ prior to each shot. The bomb was calibrated with standard benzoic acid samples supplied from Parr instruments. Standard benzoic acid samples were run each day to ensure the instrument remained in calibration. No calibration was necessary if the ΔH_c values for the combustion of pellets of benzoic acid varied < 1% from the standard reported value of 6318 cal/g.

All samples were kept at 0.25 ± 0.01 and were run in triplicate. The averages of the three runs are the values reported in the text. It should be noted that the values given in table 1 for NC, 4DNC, and 18DNC are approximations as these values are not corrected for nitrogen. The purpose of this section is to give reasonable approximations of the nitrogen content of the samples to determine what affect particle size has on the sensitivity of the material. The complete values are shown in table 1.

Table 1. Approximate heat of combustion for samples.

Sample Type	Run No.	ΔH_c (cal/g)	Sample Weight (g)
Overnight digested (18DNC)	1	2301	0.2495
	2	2238	0.2521
	3	2188	0.2516
Four-hour digested (4DNC)	1	2286	0.2551
	2	2306	0.2561
	3	2305	0.2523
Nitrocellulose (NC)	1	2269	0.2605
	2	2446	0.2571
	3	2211	0.2629
Cotton balls	1	3576	0.2549
	2	3579	0.2497
	3	3601	0.2483

3.4 Determination of Nitrogen Content

By comparing the values for the heat of combustion obtained experimentally to those of literature values obtained from nitrocellulose of known nitrogen content (11), it is possible to determine the percentage of nitrogen incorporated into the samples produced in this study. Analysis of the data showed a highly linear, inverse trend with the heat of combustion for the sample decreasing as the percent nitrogen increased. Through rearranging and solving the linear regression equation it is possible to estimate the percentage of nitrogen incorporated into the nitrocellulose.

3.5 Drop Weight Testing

Drop weight analysis was performed using an apparatus dropping a 2.5-kg hammer from a variable height onto an anvil that transports the force to the sample being analyzed. Analysis is done according to MIL-STD-1751A (16). All samples were dried in a vacuum oven at 60 °C and 0 torr for at least 2 h prior to testing. Approximately 35 ± 1 mg of sample is placed on a 0.75-in square piece of 180-grit sandpaper stored over desiccant. H_{50} values are defined as a height at which 50% of samples will undergo a reaction, and was determined according to the Langley one shot method. It should be noted that not all shots reported as go's in this test set resulted in the complete decomposition of the sample. Go's were determined if the sample underwent any kind of decomposition including, combustion, discoloration of the sample or sandpaper, smoke emission, or major distortion of the sandpaper. Standard NC had a measured H_{50} value of 17.78 in with a standard deviation of 1.508 in. The 4DNC had a measured H_{50} value of 18.67 in and a standard deviation of 2.895 in. The 18DNC had an H_{50} value of 20.15 with a standard deviation of 2.398 in. The apparent differences in the sensitivities between the acid digested samples and NC is not significant when the relatively large standard deviation of the samples is taken into account. Based on the findings from this series of tests, it is reasonable

to conclude that the acid digestion of the samples prior to nitration has little effect on the sensitivity of the material to impact.

4. Conclusions

Based on the data obtained from laboratory experiments there appears to be little distinguishable difference between the acid digested nitrocellulose and the natural NC with regards to peak decomposition temperature and vulnerability to impact events. The decomposition temperatures were found to vary less than 10 °C among all samples, with the shock sensitivity values varying less than 2 in. The advantage of the digested material comes in the particle morphology of the material. The digested material is a powder in nature and as such is much easier to handle than the NC generated from the nitration of the cotton balls which still retains a significant portion of its long strand cellulosic nature.

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